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Structure formation of integral-asymmetric membranes of polystyrene-block-poly(ethylene oxide)

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Introduction

Self-assembly of amphiphilic block copolymers offers a high potential for emerging nanotechnologies, leading to an increasing attention in recent years.

A promising application is the formation of isoporous membranes e.g. for water filtration. Various approaches are reported how to create such nanoporous films.

In the first strategy the pores are obtained by dissolving one of the components of a casted film or by edging. This procedure could also require a transfer step of the film from a solid substrate where it was prepared onto a porous support (1). However, Li et al. succeeded to prepare an ordered nanoporous composite membrane via blending polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) with Poly(acrylic acid) (PAA). The films were directly spin-coated on a porous support. By removal of the PAA from the thin top layer the permeability of the membrane could be tuned (2).

Due to special properties of PEO non-ionic amphiphilic block copolymers comprising PEO are not only of scientific interest. PEO is a water-soluble and blood compatible polymer that is characterized by its low tendency for protein adsorption (3). The self-assembly of PS-*b*-PEO in solution has been subject of scientific studies for several decades (4, 5). For thin film preparations the solvent induced assembly is widely used to produce nanodomain morphologies with controlled orientation (6-8).

The second strategy to obtain nanoporous films is based on the combination of block copolymer self-assembly and the non-solvent induced phase inversion process. This process enables the formation of integral asymmetric membranes composed of an ordered thin top layer merging into a sponge-like layer below (9-11). This offers the ability to prepare membranes with open pores without the need of transfer, edging or removal step. Furthermore this construction avoids the build-up of mechanical stresses. Recently, this process has been applied for the first time for polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) (9, 10).

The formation of these nanoporous membranes is a sensitive process strongly dependent on the self-assembly of the block copolymers in solution, the microphase separation and further stimuli e.g. temperature. Jung et al. managed to prepare an integral asymmetric membrane via combination of self-assembly of Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) and phase-inversion process (11). In order to achieve the desired structure they successfully set parameters like solvent system, evaporation time before immersion and the immersion bath temperature. These membranes have been tested for water filtration and retention properties, showing high water flux values. Furthermore the membrane was pH-responsive by reversible swelling of P2VP at low pH-values.

The aim of this work was to prepare the first integral-asymmetric membrane consisting of PS-*b*-PEO via the self-assembly of block copolymers and phase inversion process. Furthermore the properties of the membranes were characterized.

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Methods

The block copolymers used in this work have been synthesized by living sequential anionic polymerization of styrene and ethylene oxide. The membrane preparation process starting from a solution of the polymer includes: 1) hand casting of a 200 µm-thick film on a conditioned non-woven support, 2) solvent evaporation at room temperature for a defined time, 3) immersion in a non-solvent bath of a certain temperature for ca. 5 min, 4) drying at ambient conditions. The solvents for membrane casting were of p.a. grade and used without further purifications. The non-solvents were used without further purification.

Morphological characterization was mainly carried out by scanning electron microscopy using secondary electrons for the images at 3kV acceleration voltage. Samples were sputtered with Pd. Water flux measurements were carried out using a home-made testing device at transmembrane pressures up to 2 bars. Cloud-point determinations have been performed via titration with non-solvents.

Results

PS-*b*-PEO diblock copolymers with various compositions and molecular weights were prepared for the membrane preparation. In order to investigate the precipitation process of these block copolymers in various polar and non-polar solvent and non-solvent systems, cloud point determinations were carried out. This enables to create ternary phase diagrams (polymer/solvent/non-solvent). High polar non-solvents e.g. water induce the swelling of the PEO-component, leading to the suppression of the structure formation during the phase inversion process. Nevertheless, the quality of the solvent used is essential for the effective strength of the non-solvent.

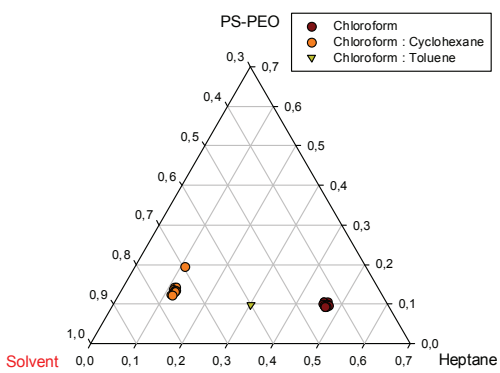

Figure 1: Ternary phase diagram of PS-*b*-PEO in different solvents, non-solvent heptane.

By reducing the quality of the solvent for PS-*b*-PEO the amount of non-solvent needed to induce the precipitation could be decreased. In case of a non-polar non-solvent system, e.g. heptane, the solvent quality could be significantly decreased by using of chloroform/cyclohexane instead of pure chloroform (Figure 1). While chloroform is a very good solvent for PS and PEO, cyclohexane appears a □-solvent for PS and poor solvent for PEO at room temperature.

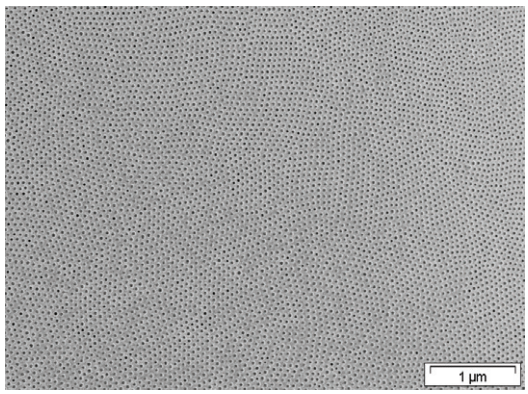

Figure 2: SEM of the surface structure of the PS-*b*-PEO block copolymer membrane.

Very regular monodisperse pores could be obtained by evaluation of non-solvent, solvent system and its evaporation time (Figure 2). These structures were found for PS-*b*-PEO block copolymers with varying compositions and molecular weights.

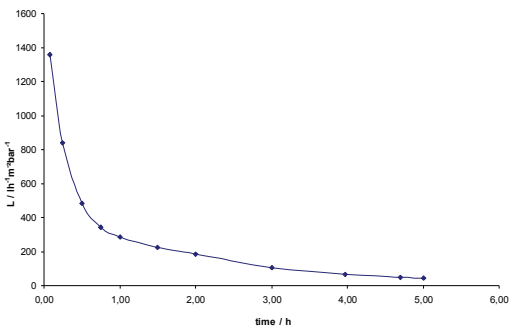

Figure 3: Water flux of the previously shown PS-*b*-PEO block copolymer membrane.

The membranes show huge water flux values at the early stages of flux measurements (> 1000 L/(m^2 h bar)). However, due to the swelling of PEO the flux reduces significantly within a short time (Figure 3). This should enable the membrane to perform a time dependent fractional filtration. Different approaches e.g. addition of salt to open the pores again were not successful. The addition of KCl increases the solubility of PEO, probably by establishing complexes similar to K^+ with crown ethers.

Discussion

PS-*b*-PEO block copolymers membranes can be produced by combination of self-assembly and phase inversion process. The membrane development required the evaluation of the non-solvent bath, solvent system and polymer concentration.

The membranes exhibit monodisperse pore size distribution on the surface. During the water flux measurement the swelling of PEO leads to closure of the pores. These membranes show a potential for temperature and time dependent fractional filtration applications.

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